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#### (19) (CA) CANADIAN PATENT (12)

- (54) MOLYBDATE-AMINE CORROSION INHIBITOR
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- (73) Granted to Dearborn Chemical Company Ltd.
  Canada
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No. OF CLAIMS 13 - NO DRAWING

### MOLYBDATE-AMINE CORROSION INHIBITOR Abstract of the Disclosure

A composition comprising a molybdate and an amine, preferably with a benzotriazole or the like added to circulating closed water systems to inhibit corrosion.

WE CLAIM:

- A corrosion inhibitor for closed aqueous systems comprising at least one molybdate and at least one amine.
- The inhibitor of Claim 1 wherein the molybdate is sodium molybdate.
- 3. The corrosion inhibitor of Claim 2 wherein said amine is selected from the group consisting of morpholine, ethylene diamine, and 2-amino-2-methyl-1-propanol.
- 4. The inhibitor of Claim 3 wherein the amine is morpholine...
- 5. The inhibitor of Claim 3 wherein the amine is ethylene diamine.
- 6. A corrosive inhibitor for closed aqueous systems comprising at least one molybdate, at least one amine, and at least one supplementary inhibitor.
- 7. The corrosive inhibitor of Claim 6 wherein said molybdate is sodium molybdate, said amine is selected from the group consisting of morpholine, ethylene diamine, and 2-amino-2-methyl-1-propanol; and said supplementary inhibitor is selected from the group consisting of benzotriazole, sodium polymethacrylate, and a copolymer of sulfonated polystyrene and maleic anhydride.
- The inhibitor of Claim 7 wherein the supplementary inhibitor is benzotriazole.
- The inhibitor of Claim 7 wherein the supplementary inhibitor is sodium polymethacrylate.
- 10. The inhibitor of Claim 7 wherein the supplementary inhibitor is a copolymer of a sulphonated polystyrene and maleic anhydride.

- 11. A method for inhibiting corrosion in closed aqueous systems which comprises introducing into said systems at least one molybdate and at least one amine.
- 12. The method of Claim 11 wherein said molybdate is sodium molybdate.
- 13. The method of Claim 12 wherein said amine is selected from the group consisting of morpholine, ethylene diamine, and 2-amino-2-methyl-1-propanol.



This invention relates to an improved corrosion inhibitor for closed water systems.

The prior art is replete with supposed inhibitors, many of which are characterized by major defects. Some of these for instance are susceptible to loss of effectiveness or breakdown due to air leakage into the water system. In this way inhibitors containing hydrazine react with oxygen and not only lose their effectiveness, but also, in many hot water heating systems tend to produce ammonia which, in the presence of oxygen, causes severe corrosion of copper and copper alloys.

Other inhibitors are susceptible to biological degradation which is a fairly common occurrence with borate-nitrite based formulas.

Some inhibitors are considered serious pollutants if a leak occurs. This is true of chromates and hydrazine. The chromates also have an undesirable yellow color and tend to stain.

Many of the prior art inhibitors require a high inorganic solids content which greatly increases the objectionable solid build-up where leaks have developed in the system and affect the performance of pump seals.

Many of the inhibitors are also incompatible with ethylene glycol treated systems.



Some inhibitors which are satisfactory for mild steel, tend to cause marked increases in corrosion rates on other metals and may produce undesirably high pH levels.

Others are degraded by heat or have various disadvantages.

In view of these various defects of the inhibitors of the prior art, it is an object of the present invention to develop a new and improved corrosion inhibitor for closed aqueous systems, which will also be satisfactory for such systems containing ethylene glycol.

A further object is an inhibitor which does not react unfavorably with oxygen or lose effectiveness, or produce corrosive effects in closed water systems, or with respect to copper and copper alloys.

An additional object is an inhibitor which is not susceptible to biological degradation, is not a serious pollutant and is non-staining.

A further object is an inhibitor which operates with a low solids content, gives full protection for conventional heat exchange metals, and is not degraded by heat.

Other objects will be appreciated from the following description of the invention:

The present invention is a new and improved corrosion inhibitor for closed water systems comprising at least one molybdate and at least one amine. These materials when mixed together and added to water inhibit the corrosion of metal in a water environment. Various combinations have been evaluated and corrosion rates determined. The results are excellent contrasted to those corrosion inhibitors known to the prior art.

In a preferred form of the invention a supplementary inhibitor is also added such as benzotriazole, sodium polymethacrylate, or a copolymer of sulphonated polystyrene and maleic anhydride.

Morpholine and ethylene diamine are preferred amines.

The invention is also valuable for use in closed agueous systems to which ethylene glycol has been added.

It is also to be noted that the molybdate anion can be easily and accurately tested, using a simple color comparison test, whether the medium used is water or ethylene qlycol and water.

As indicative of the results obtained, two types of tests were employed as shown in the following examples:

The first was a beaker test, in which the metallic coupons were stirred through a solution of the inhibitors in a tap water of medium hardness at room temperature for six days. In the second test, to evaluate the inhibitor under static conditions, the coupons were immersed in inhibited tap water in a closed nearly-filled bottle. The bottles were held at room temperature for two days, and then transferred to an oven at 70° C for a further 5 days. The following results illustrate the corrosion inhibition properties of the mixtures of sodium molybdate and amines:

EXAMPLE	
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Composition	<u>.</u>	Concent: PPM	ation	Corrosion for mild s Beaker	
1. Sodium m Morpholi Benzotri	.ne	75 152 16	) )	5.2	14.9
2. Sodium m Morpholi Benzotri	.ne Î	160 200 16	) ) )	1.7	0.0
3. Sodium m Morpholi Benzotri	.ne	250 200 16	)	0.8	-

				F	Beaker	Bottle
4.	Sodium molybdate Morpholine Benzotriazole	220 200 16	)		0.7	1.8
5.	Sodium molybdate 2-Amino-2-methyl-1-propanol Benzotriazole	220 200 16			1.0	2.0
6.	Sodium molybdate Ethylene diamine Benzotriazole	220 100 16	)		0.3	0.5
7.	Sodium molybdate Morpholine Benzotriazole Sodium polymethacrylate	220 200 16 36	)		-	0.6
8.	Sodium molybdate Morpholine Benzotriazole Sodium polymethacrylate	330 300 24 54	)		-	0.2
9.	Sodium molybdate Morpholine Benzotriazole Sodium polymethacrylate	220 200 6 36	)		0.9	2.0
10.	Sodium molybdate Morpholine Benzotriazole Sodium polymethacrylate	440 400 12 72	)		0.3	0.8
11.	Sodium molybdate Ethylene diamine Benzotriazole Sodium polymethacrylate				0.4	0.6
12.	Sodium molybdate Ethylene diamine Benzotriazole Sodium polymethacrylate	440 200 12 72	)		0.2	0.2
13.	Sodium molybdate Ethylene diamine Benzotriazole Sulphonated polystyrene	200 100 6	)		0.3	0.4
	maleic anhydride copolymer	9	)			

Benzotriazole is found to be an inhibitor for copper and copper alloys and, therefore, enhances the corrosion inhibiting properties of this formula.

Low molecular weight sodium polymethacrylate was included in the later formulations for the following reasons:

- a) It is found to inhibit, retard or prevent objectionable scale formation on high temperature heat exchange surfaces, as would be found in hot water heating systems using unsoftened make-up water.
- b) It also is found to retard crystal growth of calcium, magnesium and iron deposits. These crystalline deposits have proved to be objectionable, and are detrimental to the performance of pump seals.
- The sulphonated polystyrene/maleic anhydride copolymer was tested as an alternative to the sodium polymethacrylate.

Some of the above combinations were evaluated as corrosion inhibitors for metals other than mild steel, with the following results:

Tre	atment	<u>Level</u>	Metal_	Corrosion Beaker	Rate (mpy) Bottle
4.	Sodium molybdate Morpholine Benzotriazole	200 ) 200 ) 16 )	Copper Admiralty brass Aluminum	0.3 0.3 1.4	-
11.	Sodium molybdate Ethylene diamine Benzotriazole Sodium polymetha-	220 ) 100 ) 6 )	Copper Aluminum	0.4 3.5	2.0
	crylate	36 )			
12. Sodium molybdate Ethylene diamine Benzotriazole Sodium polymetha- crylate	Ethylene diamine Benzotriazole	440 ) 200 ) 12 )	Copper Aluminum	0.4 8.0	- 5.6
	72 )				
9.	Sodium molybdate Morpholine	440 ) 400 )			
	Benzotriazole Sodium polymetha- crylate	12 )	White brass	0.1	1.6
		72 )	Aluminum	2.1	9.9
10.	Sodium molybdate Morpholine Benzotriazole Sodium polymetha-	440 ) 400 ) 12	White brass Aluminum	0.1	1.6 9.9
	crylate	72)			

The preferred treatment is No. 9 (and No. 10, which is a double dose of No. 9), in that it is less aggressive towards aluminum in a flowing system than the formula based on ethylene diamine instead of morpholine (No. 11 and No. 12).

Finally, corrosion rates, using treatments No. 9 and No. 10, were determined for mild steel using 50% ethylene glycol, 50% tap water as the cooling medium. The rates were as follows:

Treatment No. 9 0.4 mpy (beaker) & 1.0 mpy (bottle)
Treatment No. 10 0.4 mpy (beaker) & 0.3 mpy (bottle)

These results indicate that the same inhibition of corrosion can be achieved in ethylene glycol/water mixtures as can be achieved in water alone.

It will be appreciated that many variations can be made without departing from the principles of the invention.

## SUBSTITUTE REMPLACEMENT

# SECTION is not Present Cette Section est Absente